

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date  
26 May 2005 (26.05.2005)

PCT

(10) International Publication Number  
**WO 2005/048293 A2**

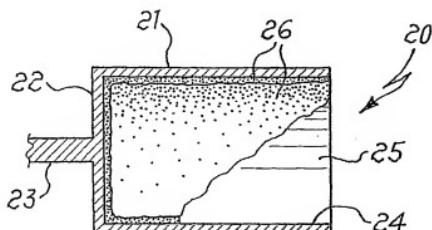
- (51) International Patent Classification<sup>7</sup>: **H01J 61/06**, (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (21) International Application Number: PCT/IT2004/000614
- (22) International Filing Date: 9 November 2004 (09.11.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: MI2003A002208 14 November 2003 (14.11.2003) IT
- (71) Applicant (*for all designated States except US*): SAES GETTERS S.P.A. [IT/IT]; Viale Italia, 77, I-20020 Lainate MI (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): CORAZZA, Alessio [IT/IT]; Via Rienza, 72, I-22100 Como (IT). MASSARO, Vincenzo [IT/IT]; Via Livio Andronico, 35, I-74100 Taranto (IT).
- (74) Agents: ADORNO, Silvano et al.; Società Italiana Brevetti S.p.A., Via Carducci, 8, I-20123 Milano (IT).
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATHODE WITH INTEGRATED GETTER AND LOW WORK FUNCTION FOR COLD CATHODE LAMPS



(57) Abstract: There are disclosed several embodiments of a cathode (11; 20; 30) for cold cathode lamps having the surface at least partially coated with a layer of a getter material (15; 26; 31), which allows to achieve a reduction of the value of the work function of the cathode and therefore a reduction of the power consumption of the lamp.

**WO 2005/048293 A2**

"CATHODE WITH INTEGRATED GETTER AND LOW WORK FUNCTION  
FOR COLD CATHODE LAMPS"

5       The present invention relates to a cathode for cold cathode lamps, having an integrated getter and with a reduced value of the work function, which allows to decrease the power consumption of the lamps wherein it is used.

Cold cathode lamps are a kind of discharge lamps. Discharge lamps are all those lamps wherein the light emission takes place as a consequence of the electric discharge in a gas means. The discharge is triggered and supported by the 10 potential difference applied to two electrodes (called cathodes) placed at the opposite ends of the lamp. The family of discharge lamps comprises also the so called hot cathode lamps, but the cold cathode ones are preferable because they last much longer (40.000 – 50.000 operation hours against 12.000 – 15.000 of the hot cathode lamps).

15      The cathodes of cold cathode lamps may be shaped as a metal strip or metal full cylinder. The preferred geometry is however the hollow one: in this case the cathode has the shape of a hollow cylinder, open at the end facing the discharge zone and close at the opposite end. As well known in the field, a first advantage of hollow cathodes with respect to other shapes of cathodes is a lower potential 20 difference (of about 5 – 10%) required for lamp functioning; another advantage is a lower intensity of the "sputtering" phenomenon of the cathode, that is the emission of atoms or ions of the material of the cathode which may deposit on adjacent surfaces, among which the glass walls of the lamp, reducing the light output of the latter. The hollow cathodes are particularly suitable for being used in 25 miniaturized lamps, as for example lamps for the back-lighting of liquid crystal displays (commonly known as LCDs). Examples of lamps with hollow cathodes are disclosed for example in patents US 4,437,038 and US 4,885,504 and in the publication of the Japanese patent application 2000 – 133201.

When a cold cathode lamp is turned on, the first electron emission occurs 30 thanks to the electric field, which, if sufficiently high, is capable of extracting electrons from the material forming the cathode; typical values of potential

difference to be applied to the electrodes of hollow cathode lamps for the ignition thereof are of the order of thousands of volts (V), for example between about 1000 and 2000 V; this ignition voltage is known in the field as "starting voltage". When the discharge has been started (normally after less than one second), the cathodes 5 become hot and also the thermoionic effect contributes to the emission. While the lamp is working, the potential difference to be supplied to the cathodes sets to values of a few hundred volts, for example between about 300 and 600 V.

The power consumption of lamps is in any case related to the energy value required for extracting electrons from the material of the cathodes, both in the 10 ignition phase and when the discharge has established; this energy value is known as "work function", indicated in literature with the Greek letter  $\Phi$ , and is a typical value of each single material (even if it can vary in relation with some parameters such as the crystalline face wherefrom the electrons are emitted, or the contamination state of the emitting surface). In the end, the power consumption of 15 a lamp depends directly on the work function of its cathodes.

The cathodes of cold cathode lamps may be made of metals such as niobium and tantalum, that have both however too high prices for practical use; tungsten, having values of work function comprised between about 4,2 and 4,6 electronvolt (eV); nickel, with values of work function comprised between about 4,7 and 5,3 20 eV; or, more commonly, molybdenum, which has values of work function comprised between about 4,4 and 4,9 eV. In the case of hollow cathodes, especially of small dimensions, the metal used shall have good characteristics of mechanic malleability: tungsten is practically not used for these cathodes, while molybdenum has industrial application, but because of the difficulty of working, 25 the cathodes made of this metal are rather expensive. Nickel may thus result preferable since it has a good malleability and a low cost, even if it has the disadvantage of the relatively high values of the work function.

The reduction of power consumption is a constant need of manufacturers of lamps or devices wherein these are used, both in fixed and, above all, portable 30 applications, wherein energy is supplied by batteries or accumulators which have a finite energy reserve. In the case of portable computers, for example, the screen

is generally of LCDs type, retro-illuminated by one or two linear cold cathode fluorescent lamps with a diameter of a few millimeters; the illumination of the screen is the greater contribution to the consumption of the accumulator of the computer, limiting the hours of autonomy. LCD screens for other applications (for 5 example domestic television screens) may comprise from four to ten fluorescent lamps.

To reduce the work function of the cathodes, and thus the power consumption of the lamps, it is known to deposit on the surface of the same cathodes an emissive material, with a work function lower than that of the 10 underlying metal.

Another necessity of the cold cathode lamp manufacturers is to ensure a constant composition of the atmosphere wherein the discharge takes place. As a matter of fact, it is known that some impurities alter the working characteristics of the lamps: for example, oxygen may seize the mercury necessary for the working 15 of the fluorescent lamps, while hydrogen may alter the electric parameters of the discharge, in particular by increasing the starting voltage. For this purpose, it is known to add inside the lamps a getter material, that is a material capable of chemically bind the impurities present in the gas wherein the discharge takes place. Getter materials widely used for this purpose are for instance the alloys 20 zirconium-aluminum disclosed in patent US 3,203,901; the alloys zirconium-iron disclosed in patent US 4,306,887; the alloys zirconium-vanadium-iron disclosed in patent US 4,312,669; and the alloys zirconium-cobalt-mischmetal disclosed in patent US 5,961,750 (mischmetal, also indicated as MM in the following, is a mixture of Rare Earth metals with the possible addition of yttrium and/or 25 lanthanum).

Even if in some cases the getter is introduced in the lamp simply in the shape of a pill formed only of the powders of the material, it is much more preferable that it be in the shape of a device wherein the getter material is present in a container or on a metallic support, and that said device is fastened to any 30 constituting element of the same lamp: the reason is that a non fastened getter is not generally in the hot areas of the lamp and thus its gas sorption efficacy

decreases, and moreover it may interfere with the luminous emission. An example of getter device for lamps is disclosed in patent US 5,825,127. The getter device may be for example fastened (normally with welding spots), to the support of the cathode, while in some cases a dedicated support is added to the lamp: in any 5 case, anyway, additional steps are required in the manufacturing process of the lamp. Furthermore, in the case of miniaturized lamps such as those used to back-light LCDs, it is difficult to find a suitable arrangement for the getter device inside the lamp, and the assembling operations of the device may result extremely difficult. The international patent application WO 03/044827, in the name of the 10 applicant, discloses a hollow cathode wherein the getter material is directly deposited on some areas of the surface of the cathode itself; according to the teaching of this international application, the getter material may be chosen among titanium, vanadium, yttrium, zirconium, niobium, hafnium and tantalum, or among the alloys based on zirconium or titanium with one or more elements 15 chosen among the transition metals and aluminum.

European patent application EP-A-0675520 discloses a hollow cathode whose interior is partially coated with a deposit constituted of powders of alumina and zirconium, the first having the function of decreasing the work function of the cathode and the second having the function of getter for the impurities. The 20 deposit is formed by partially dipping the metallic cylinder which constitutes the structure of the cathode in a paste containing the mentioned materials in a suspending means made of a water-acetone mixture containing a binding material. According to the teaching of this document, only the internal side of the cathode is coated, in order to avoid the sputtering of the material of the emissive mixture that 25 would occur if this was present even on the outer surface. Furthermore, for the same reason, it is preferable to avoid the presence of the emissive deposit also in an internal area of the cathode corresponding to a cylindrical surface at the end of the cathode turned towards the inner of the lamp. The deposits formed through this way have, however, the problem of a not negligible loss of powders, which 30 causes a degradation of the functionality of the cathode with time.

The object of the present invention is to provide a solution to the above

described problems. In particular, an object of the present invention is to provide a cathode at least partially coated with a deposit of a single material, which allows to decrease the power consumption of the lamps wherein the cathode is inserted and to integrate the getter function.

5 This object is achieved with a cathode for cold cathode lamps, at least partially coated with a getter material comprising a metallic bearing part at least partially coated with a layer of getter material, characterized in that said getter material is chosen among:

- 10 - alloys comprising zirconium, cobalt and one or more components selected among yttrium, lanthanum or rare earths such that, in the ternary diagram of weight % compositions, they are enclosed in the polygon defined by the points:
- a) Zr 81% - Co 9% - A 10%
  - b) Zr 68% - Co 22% - A 10%
  - c) Zr 74% - Co 24% - A 2%
  - d) Zr 88% - Co 10% - A 2%
- 15 wherein A is an element selected among yttrium, lanthanum, rare earths or mixtures thereof;
- 20 - alloys consisting of yttrium and aluminum containing at least 70% by weight of yttrium; and
- 25 - alloys consisting of yttrium and vanadium containing at least 70% by weight of yttrium.

The invention will be further described with reference to the drawings wherein:

- 25 - Fig. 1 shows a cut-out view of the end of a lamp wherein a cathode of the invention is present;
- Figs. 2 and 3 show a sectional view of two cathodes according to one preferred embodiment of the invention;
- Figs. 4 and 5 show graphs representing the gas sorption characteristics of 30 two cathodes according to the invention.

The inventors have found that a cathode at least partially coated with a

getter material formulated as described, besides integrating the getter function on the cathode, achieves also the effect of decreasing the energy required for the emission of electrons, through the decreasing of the work function of the cathode itself.

- 5        The deposition of getter material according to the invention may be advantageously accomplished on cathodes of any geometry, for example strip shaped, full or hollow cylinder shaped.

Figure 1 shows a cut-out view of the end of a lamp, 10, containing a cathode 11; it is exemplified the case in which the cathode is a simple metal strip, 12, 10 obtained by tapering a metallic wire 13 passing through the glass of the bottom wall 14 of the lamp. A fraction of the surface of the strip 12 is covered with a getter material of the invention, 15. A cathode completely analogous to that of figure 1, but full cylinder shaped, may be obtained coating with getter material the end of wire 13 without previously tapering it.

- 15      As said before, the preferred shape for the cathode is the hollow one. As it is known, in the hollow cathodes the discharge takes place mainly inside the cavity, therefore it is necessary that it is the coated part, while the outside of the cathode may be coated or not. Coating also the outside has the advantage to increase the quantity of getter material, and thus the removal capacity of impurities from the 20 internal atmosphere of the lamp; since in hollow cathodes the discharge takes place mainly inside the cavity, the fraction of getter material on the outer surface of the cathode performs mainly the gettering function, while the material inside performs also the function of decreasing the work function of the cathode. In figures 2 and 3, which illustrate only the cathode in section, are shown two 25 possible embodiments of hollow cathodes according to the invention. Cathode 20 is formed of a cylindrical part 21 with a close end 22 to which a brace 23 is fastened, which generally is a metallic wire soldered in the glass of the end of the lamp as shown in the case of figure 1; the inner surface of the cathode, 24, which defines the cavity 25, is coated with getter material 26; in order to show some 30 details, in figure 2 is shown a partial coating of surface 24, but this coating is to be meant complete. The preferred material for producing the metallic part of the

cathode is nickel, which is easily mechanically worked; the backing wire 23 is preferably made of materials which have a thermal expansion similar to that of the glasses of the envelope of the lamp, in order to reduce the risks of breaking the glass, because of thermal shocks, during the sealing and the on/off phases of the  
5 lamp; a possible material is molybdenum. Brace 23 may be fastened to part 22 for example through soldering or crimping.

In the case of cathode 30, the coating with getter material 31 is present both inside the cavity and on the external surface of the metallic part 32; as for the rest this cathode is completely analogous to that of figure 2.

10 A getter material useful in the present invention are the alloys described in patent US 5,961,750 in the name of the applicant. Particularly preferred is the use of the alloy having the weight per cent composition Zr 80% - Co 15% - MM 5%, produced and sold by the applicant under the name St 787. Mischmetal is the trade name of several mixtures of Rare Earths which may have different formulations:  
15 generally the elements present in greatest quantity are cerium, lanthanum and neodymium, with smaller quantity of other Rare Earths. Anyway, the exact composition of the mischmetal is not important, since the above mentioned elements have similar chemical behavior, so that the chemical attitude of the different types of mischmetals is essentially the same as the content of the single  
20 element varies.

Other getter materials useful for the present invention are Y-V or Y-Al alloys containing at least 70% by weight of yttrium, that are particularly efficient to decrease the hydrogen partial pressure in the final lamps.

The layer of getter material may have a thickness comprised between a few  
25 microns ( $\mu\text{m}$ ) and a few hundreds  $\mu\text{m}$ , depending on the technique used to produce it (as specified in the following). In the case of hollow cathodes, this thickness is also a function of the diameter of the cavity: in the case of cathodes with cavity of diameter of about one millimeter, it is preferable that the thickness of the getter layer is as low as possible, provided that there is enough getter  
30 material to perform efficiently the impurities sorption function.

The layer of getter material (26; 31) may be deposited on the metallic part of

the cathode through different ways.

- According to a first embodiment, the layer of getter material may be obtained through cathodic deposition, technique better known in the field of thin films manufacturing as "sputtering". As known, in this technique in a suitable chamber are arranged the support to be coated (in this case the hollow cathode) and a generally cylindrical body, called "target", of material of which the layer is to be obtained; vacuum is made in the chamber and then a rare gas, usually argon, is introduced at pressures of about  $10^{-2}$  –  $10^{-3}$  mbar; applying a potential difference between the support and the target (the latter kept at cathodic potential)
- 5      a plasma is created in argon, with formation of ions Ar<sup>+</sup> which are accelerated by the electric field toward the target, thus eroding it by impact; the particles removed from the target (atoms or "bundles" of atoms) deposit on the available surfaces, among which those of the support, thus forming a thin layer; for further details about principles and instruction for use of the technique it is to be referred
- 10     to the wide literature of the field. The productivity of the sputtering technique, as thickness of the layer deposited in a time unit, is not very high, therefore this technique may be preferred when getter layers of thickness not higher than 20  $\mu\text{m}$  have to be produced, and thus for example in the case of hollow cathodes of small diameter. Partial coating of the surfaces of the metallic part of the cathode may be
- 15     obtained in this case using suitable supports of said parts which, during the sputtering process, carry out also the masking thereof: for example, the cathode of figure 2 may be manufactured using, during the sputtering, a cylindrical support inside which the hollow cathode to be coated is arranged, and so that said support is in contact with the external surface of the cylindrical part 21, leaving thus only
- 20     25     surface 24 exposed.

Another method for manufacturing a cathode with a coating of getter layer according to the invention is through the electrophoretic technique; the principles of manufacturing getter material layers through this way are disclosed in patent US 5,242,559 in the name of the applicant, to which it is to be referred for further 30     details about the technique. In this case the partial or total coating of the metallic part of the cathode may be simply obtained by immersing partially or totally said

part in the coating bath, and also in this case it is possible to coat selectively one of the two surfaces, internal or external, by using a suitable support of said metallic part. This technique is suitable for manufacturing getter layers thicker than those obtained by sputtering, with the opportunity to form easily and rapidly 5 layers of thickness up to a few hundreds  $\mu\text{m}$ .

Finally, another available technique is the spray one, wherein a getter particles suspension in a suitable liquid means is used, the suspension is sprayed on the part to be coated through a compressed gas (generally air) and the so obtained deposit is dried and solidified through thermal treatments. The use of the 10 technique to obtain getter deposits is disclosed for example in patent US 5,934,964 in the name of the applicant.

The invention will be further illustrated by the following examples.

#### **EXAMPLE 1**

A layer about 1  $\mu\text{m}$  thick of an alloy containing zirconium, cobalt and 15 mischmetal is produced on a tungsten wire. The layer is obtained through sputtering starting from a target of the St 787 alloy; as known in the field, different elements have different sputtering yields, so that starting from a multicomponent target the final composition of the obtained layer is generally different from the target one; in this case, the layer obtained on tungsten wire has 20 a composition which, compared to that of the St 787 alloy, is enriched in zirconium and poorer in cobalt. On the so obtained wire is effected a measure of the work function, according to ASTM F 83-71 standard procedure; in particular it is followed the second available way according to this procedure, known as "Schottky method". Also the work function of a fragment of the same tungsten 25 wire is measured, in this case however without the coating according to the invention.

The two tests produce as a result a value of work function,  $\Phi$ , of about 4,5 eV for the uncoated tungsten, and of about 3 eV for the coated wire according to the invention, with a decrease of the  $\Phi$  value of about 33%. The value of about 4,5 30 eV measured for the uncoated wire agrees with the values in the range 4,2-4,6 eV given in literature, confirming that the measurements have been carried out

accurately.

#### EXAMPLE 2

The test of example 1 is repeated, with the difference that in this case the tungsten filament is covered with an yttrium-vanadium alloy film, produced by  
5 sputtering starting with a target of weight percent composition Y 96% - V 4%.  
The value of work function measured is about 3,1 eV, with a reduction of about 30% compared to pure tungsten.

#### EXAMPLE 3

The test of example 1 is repeated, using this time a nickel filament,  
10 measuring the  $\Phi$  value on a fragment of the pure metallic wire and on a fragment  
of the same wire coated by sputtering starting from a target of St 787 alloy. In this  
case the values obtained are of about 4,9 eV for the uncoated nickel and of about  
3,1 for the coated wire according to the invention, with a reduction of the  $\Phi$  value  
of about 37%. Also in this case the  $\Phi$  value measured on nickel agrees with the  
15 values given in literature, which are in the range 4,7 – 5,3 eV.

#### EXAMPLE 4

A specimen comprising a tungsten wire coated with a film of St 787 alloy  
produced as described in example 1 is subjected to a hydrogen sorption test. The  
specimen is introduced into a glass bulb, the bulb is evacuated, and the specimen  
20 is activated by heating at 400 °C during 30 minutes (by induction through a coil  
placed outside the glass bulb); the specimen is then allowed to cool down to 25 °C  
and the test is carried out by following the procedure described in standard ASTM  
F 798-82, with a hydrogen pressure of  $4 \times 10^{-6}$  mbar. The test results are reported  
in a graphic as curve 1 in figure 4, as sorption velocity (indicated with S and  
25 measured in cubic centimeter, cc, of gas sorbed per second, normalized per square  
centimeter of alloy) as a function of the quantity of sorbed gas (indicated with Q  
and measured in cubic centimeter of gas multiplied by the pressure of measure in  
attoPascal, hPa, and normalized per square centimeter of alloy).

#### EXAMPLE 5

30 The test of example 4 is repeated, using this time carbon monoxide as the  
test gas. The test results are reported in a graphic as curve 2 in figure 4.

**EXAMPLE 6**

A specimen comprising a tungsten wire coated with a film of an Y-V alloy produced as described in example 2 is subjected to a hydrogen sorption test. The specimen is introduced into a glass bulb, the bulb is evacuated, the specimen is  
5 activated by induction heating at 500 °C during 10 minutes and then allowed to cool down to 25 °C; the hydrogen sorption test is carried out as in example 4. The test results are reported in a graphic as curve 3 in figure 5.

**EXAMPLE 7**

The test of example 6 is repeated, using this time carbon monoxide as the  
10 test gas. The test results are reported in a graphic as curve 4 in figure 5.

The tests confirm that the coating of a metallic cathode with a getter according to the invention allows to decrease notably the value of the work function of the cathode; the cathodes of the invention also show good gas sorption properties, as resulted by the tests of examples 4 to 7.

## CLAIMS

1. A cathode (11; 20; 30) for cold cathode lamps with integrated getter and with a reduced value of the work function, comprising a metallic bearing part (12; 21; 22; 32) at least partially coated with a layer of getter material (15; 26; 31), characterized in that said getter material is chosen among:
  - alloys comprising zirconium, cobalt and one or more components selected among yttrium, lanthanum or rare earths such that, in the ternary diagram of weight % compositions, they are enclosed in the polygon defined by the points:
    - a) Zr 81% - Co 9% - A 10%
    - b) Zr 68% - Co 22% - A 10%
    - c) Zr 74% - Co 24% - A 2%
    - d) Zr 88% - Co 10% - A 2%
  - alloys consisting of yttrium and aluminum containing at least 70% by weight of yttrium; and
  - alloys consisting of yttrium and vanadium containing at least 70% by weight of yttrium.
2. A cathode according to claim 1 wherein said metallic bearing part is made of a metal chosen among nickel, molybdenum, tungsten, niobium and tantalum.
3. A cathode according to claim 2 wherein said metallic bearing part has the shape of a strip, a full cylinder or a hollow cylinder.
4. A method for manufacturing a cathode according to claim 1 wherein the getter material layer is formed through cathodic deposition.
5. A method according to claim 4 wherein said getter material layer has a thickness lower than 20  $\mu\text{m}$ .
- 30 6. A method according to claim 4 wherein the metallic bearing part (21, 22; 32) has the shape of a hollow cylinder and the partial coating of one or both

the internal and external surfaces of said part takes place through masking during the cathodic deposition with a suitably shaped support element.

7. A method for manufacturing a cathode according to claim 1 wherein the getter material layer is formed through electrophoretic deposition.

5 8. A method according to claim 7 wherein the partial coating of one or both the internal and external surfaces of said hollow cylindrical part takes place through partial immersion in a liquid suspension containing getter particles used for the deposition and possible masking of one of said surfaces.

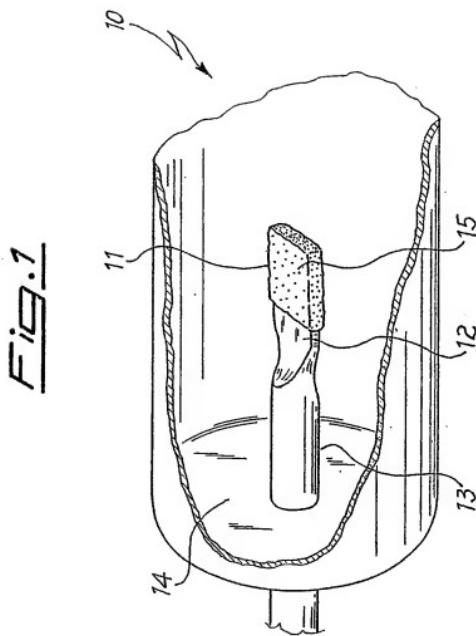
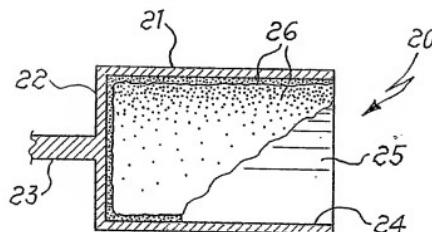
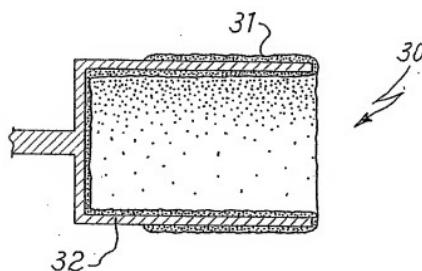


Fig. 2Fig. 3

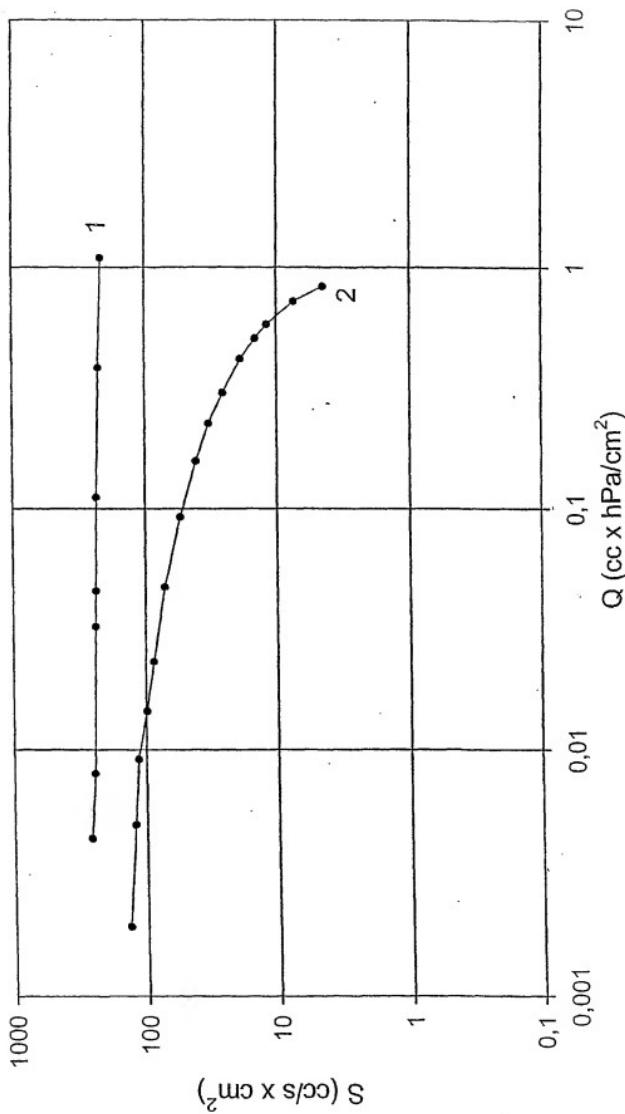
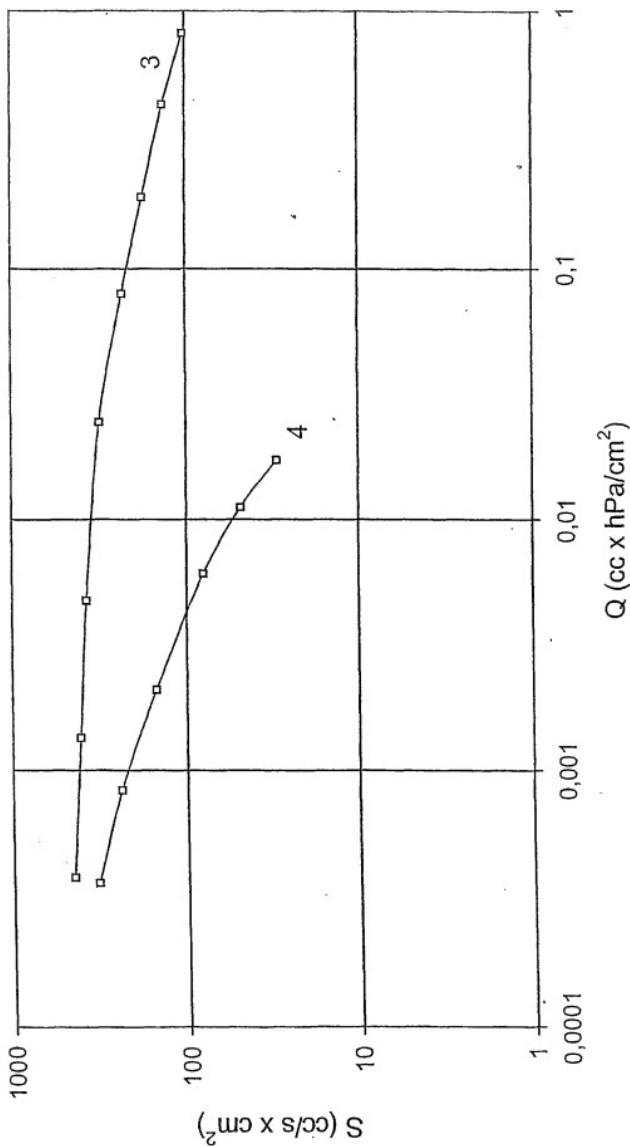


Fig. 4



**Fig. 5**